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ZnO/mesoporous silica nanocomposites prepared by the reverse micelle and the colloidal methods: Photoluminescent properties and quantum size effect

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Abstract

Quantum size effect was demonstrated in ZnO/mesoporous silica nanocomposites prepared by two different routes: the reverse micelle strategy and the colloidal method owing to a fine tuning of particles grown by the control of mesopore size. N₂ adsorption–desorption measurements, Atomic Absorption and Photoluminescent spectroscopy have evidenced the efficient loading and growth of ZnO nanoparticles in the channels of the mesoporous silica matrix. The present work illustrated that both methods are quite efficient in the preparation of short wavelength (blue) laser nanocomposite.

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1. Introduction

Optoelectronic nanocomposites are a new class of materials which exhibit very interesting and particular properties and attract a growing attention due to their potential applications in information storage and optoelectronic devices. This kind of nanocomposites are usually composed of two phases which are generally a semiconductor and an inorganic matrix [1]. The size of the semiconductor due to the matrix effect is in the nanometric size range resulting in quantum size effect (QSE) which can lead to the enhancement of the band gap of the semiconductor [2]. Consequently, the emission wavelength of the semiconductor is blue-shifted, which is very relevant for the short wavelength design. However, the conception of optoelectronic nanocomposites still remains a great challenge since it is very difficult to obtain a particle size of semiconductor as

desired while preventing the aggregation of the nanoparticles.

Very recently, we have demonstrated a very efficient quantum size effect and an important blue shift in the PL emission of ZnO/Faujasite X optoelectronic nanocomposites [3,4]. It was shown that the ZnO nanoparticles were grown inside the 3D-channels of the Faujasite X without destruction of the crystalline structure of the zeolite. However, some modifications of the symmetry were observed due to the effective presence of the ZnO nanoparticles.

Discovered in 1992 [5], silica mesoporous materials have successfully been used in the conception of optoelectronic nanocomposites [6,7] and considered as very promising matrix because their channels, with diameter ranging from 2 to 10 nm, can limit the size of the semiconductor nanoparticles during their growth. In 2001, our laboratory has reported the preparation of highly ordered silica mesoporous materials CMI-1 with hexagonal structure of the mesochannels [8] by employing a neutral surfactant which allows a soft removal of the templating agent by simple ethanol extraction. This synthesis pathway is expected to prepare pure siliceous mesoporous materials with struc-

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tural and surface defects as less as possible. Preliminary PL studies of CMI-1 mesoporous materials have clearly shown the absence of the 1.9 eV PL band usually observed in amorphous SiO₂ and associated with oxygen vacancies [9]. The absence of these defects is crucial for the preparation of optoelectronic materials using silica as matrix since the optical transparency in visible light range is the primary condition. This confirmed our expectation that CMI-1 mesoporous materials are ideal matrix for the preparation of optoelectronic nanocomposites.

ZnO is of particular interest due to its large band gap value (3.37 eV) and its important exciton binding energy (60 meV) [10,11] which allows the excitonic emission to be quite significant even at room temperature (25 meV) [12]. Our recent studies have revealed for the first time a strong two-photon random lasing effect arising from the stimulated emission of ZnO nanoparticles confined inside the silica mesoporous CMI-1 matrix [13]. The mechanism of lasing implies the scattering of the stimulated emission within the mesoporous matrix where active ZnO nanoparticles were grown [14].

ZnS nanoparticles have also been incorporated into CMI-1 matrix and the obtained nanocomposite has shown very efficient quantum size effect resulting in an important blue shift of the PL emission due to the nanometric size of the ZnS particles [15]. However, the distribution of ZnO and ZnS nanoparticle sizes is still relatively broad and the improvement of the homodispersity could be achieved only by the development of more efficient methods to control the nanoparticle growth during their incorporation.

This Letter deals with two different but original pathways to load ZnO nanoparticles inside the channels of mesoporous silica materials, the reverse micelle and the colloidal method. The rapid growth of particles in size in colloidal solution is followed and the PL properties have been studied. The present letter reports our continued effort in the conception of optoelectronic nanocomposites.

2. Experimental

2.1. Synthesis

The reverse micelle method implies the preparation of a ZnO reverse micelle solution by dissolving 33.3 g of NaAOT (sodium bis(2-ethylhexyl)sulfosuccinate) in a water/iso-octane solution containing Zn(ClO₄)₂ and NaOH [16]. After homogenization, 0.5 g of the reverse micelle solution was slowly added in a micellar solution (Brij56 10% in water) at 70 °C. To this mixture of two surfactants, the silica source (tetramethoxysilane) was introduced dropwise. After the hydrothermal treatment, the ethanol extraction and calcinations under N₂ and then O₂ were carried out in order to remove the surfactant molecules.

For the colloidal method, a mesoporous silica material was firstly synthesized as described elsewhere [8]. A ZnO colloidal suspension was prepared by mixing Zn(ClO₄)₂ and NaOH aqueous solutions in ca. 90 ml of methanol under vigorous stirring [17]. 0.5 g of the mesoporous silica was impregnated with this colloidal solution during 30 s and was then immediately filtered and washed several times with methanol.

These two synthesis strategies are illustrated in Fig. 1.

2.2. Characterization

Nitrogen adsorption–desorption isotherms were obtained at 77 K over a wide relative pressure range from 0.01 to 0.995 with a volumetric adsorption analyzer TRI-STAR 3000 manufactured by Micromeritics. The sample was degassed further under vacuum for several hours at 320 °C prior to nitrogen adsorption measurements. The pore diameter and the pore size distribution were determined by the BJH (Barret, Joyner, Halenda) method [18]. Small-angle X-ray diffraction patterns were recorded with

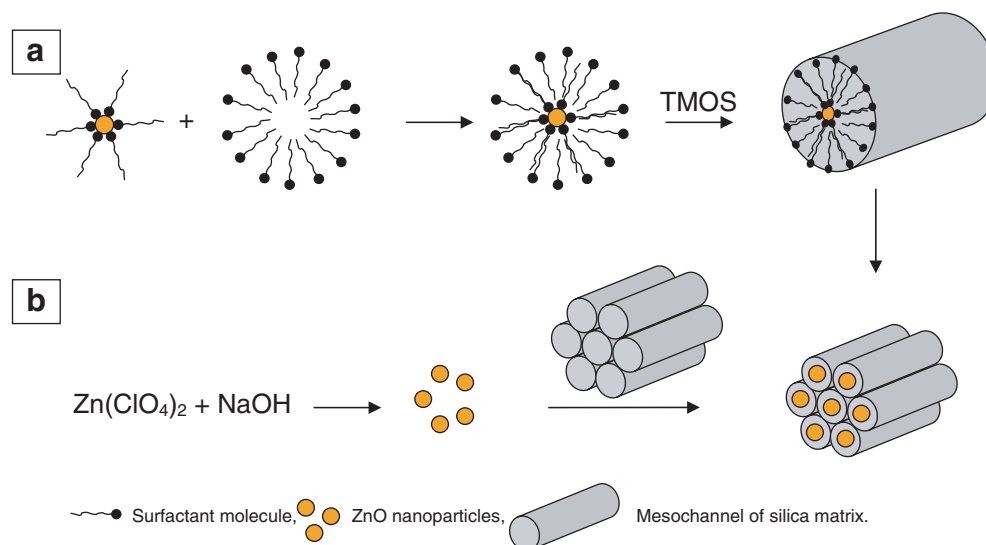


Fig. 1. The preparation of nanocomposites by the reverse micelle method (a) and the colloidal method (b).

a Panalytical X'Pert diffractometer equipped with a copper anode producing X-rays with a wavelength equal to 1.54178 Å. The morphology of the obtained mesoporous materials was studied using a Philips XL-20 scanning electron microscope (SEM) with sample preparation by metalisation. Photoluminescent spectra were recorded at room temperature with an ArF laser (193 nm, 6.4 eV) as the excitation source and an iCCD camera as detector. The laser beam was focused onto the sample with a spot size of $1.36 \times 10^{-2} \text{ cm}^2$.

3. Results and discussion

3.1. Reverse micelle method

The general characterization of the sample prepared by the reverse micelle method is presented in Fig. 2. N_2 adsorption–desorption isotherm is type IV [19], characteristic of mesoporous materials (Fig. 2a), surface area is very high ($880 \text{ m}^2/\text{g}$) and the pore size distribution is centered at 2.8 nm (Fig. 2b). Small-angle XRD study revealed only one broad diffraction peak within the 2θ range 1.0 – 5.0° , indicating that the mesopores are not periodically organized (Fig. 2c). Nevertheless, the observation of this diffraction peak can be correlated with the regular repetition of the pore diameter with a very good homogeneity. The particle

morphology was studied by scanning electron microscopy. The micrograph of Fig. 2d reveals that the sample prepared by the reverse micelle method exhibits undefined morphologies made of blocks and very small particles.

PL studies point out a complex emission spectrum composed of one very broad band in the range of 2.5–5.5 eV (Fig. 3a). Our recent work about the PL properties of mesoporous silica CMI-1 can help us to discriminate the origin of these emission bands [9]. Usually, with the 6.4 eV excitation, three contributions, at 3.0, 4.0 and 4.3 eV, can be observed in the PL spectrum of a pure CMI-1 material, which are attributed to surface defects associated with silanol groups. The first one, at ca. 3.0 eV, is ascribed to E' centers ($\equiv\text{Si}^\cdot$) while the second, at ca. 4.0 eV, is believed to come from $\equiv\text{Si}-\text{O}_2^\cdot$ centers. The origin of the third PL band, at 4.3 eV, is not clear but is thought to come also from silanol groups. After a Gaussian decomposition strictly on the basis of the physical principle and according to the PL properties of ZnO and SiO_2 species, four emission bands at 3.0, 3.6, 4.0 and 4.3 eV can be distinguished. Three bands at 3.0, 4.0 and 4.3 eV can be immediately attributed to mesoporous silica matrix. The last PL band is relatively wide and centered at 3.6 eV. This emission can obviously be assigned to ZnO nanoparticles grown inside the channels of the CMI-1 matrix by the reverse micelle method (0.5 wt.% loading). This PL band is blue

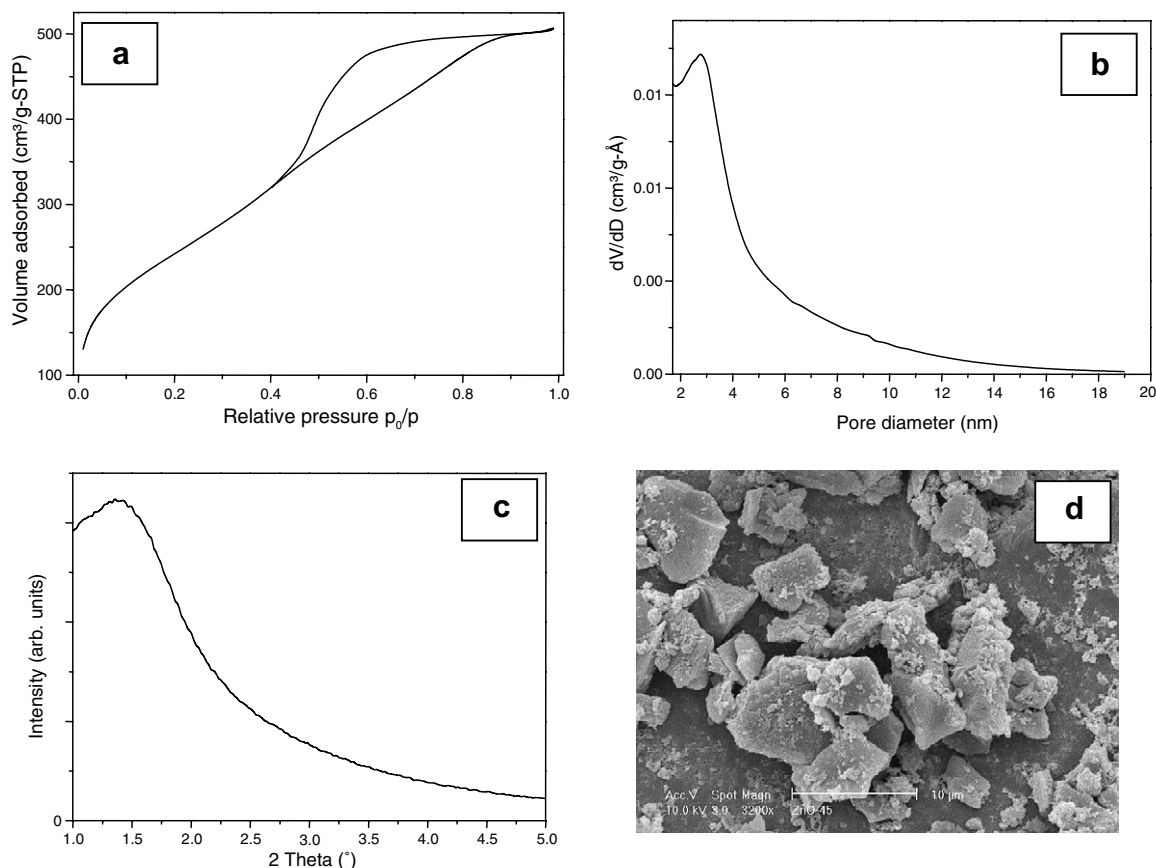


Fig. 2. Textural (a) and (b), structural (c) and morphologic (d) properties of ZnO/mesoporous silica prepared by the reverse micelle method.

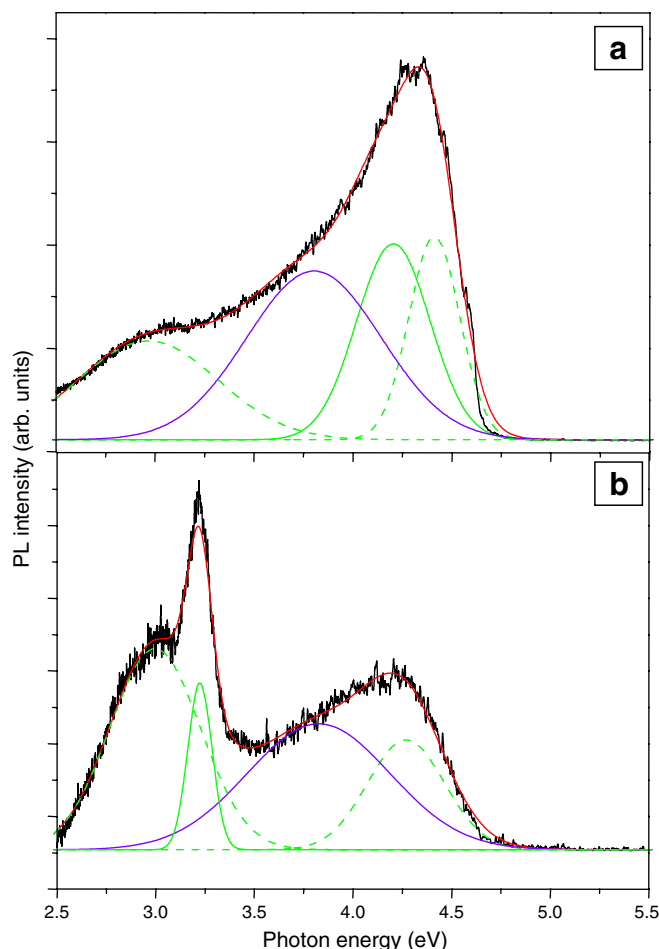


Fig. 3. PL spectrum of ZnO/mesoporous silica nanocomposite prepared by the reverse micelle method (a) and the colloidal method (b) (excitation wavelength = 193 nm).

shifted in comparison to bulk ZnO (3.3 eV), indicating that the channels of the CMI-1 matrix have an efficient limitation effect on the size of ZnO nanoparticles during their growth. This part of the work demonstrates clearly that by the reverse micelle method, we can well control the ZnO particle size and prepare short wavelength (blue) laser nanocomposites. Our further work of this part is to increase the ZnO loading to enhance the intensity of the blue-shifted band emission.

3.2. Colloidal method

Prior to the incorporation of ZnO nanoparticles inside the CMI-1 matrix, we have prepared a ZnO colloidal solution and performed fluorescence measurements to follow the growth of the colloids (Fig. 4). The excitation wavelength was 300 nm. In the first minutes, the emission of the ZnO solution is blue shifted in comparison to bulk ZnO and this blue shift disappears quickly after 15 min measurements, indicating that the particles of ZnO are large enough to behave as bulk ZnO. This first study on the growth of ZnO in a colloidal solution demonstrated

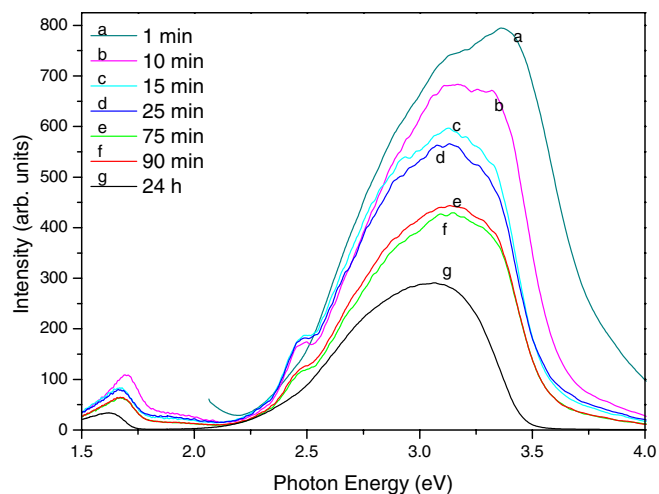


Fig. 4. Evolution of the PL spectra of the ZnO colloidal solution with time (excitation wavelength = 300 nm).

the instability of this colloidal solution and the spontaneous aggregation of ZnO nanoparticles. It also suggests that the CMI-1 matrix must be impregnated inside the ZnO colloidal solution as soon as the ZnO colloidal solution is prepared to ensure that the ZnO nanoparticles are small enough to enter the mesochannels.

On the basis of above work, the impregnation time of CMI-1 silica matrix in the colloidal solution was fixed at 60 s.

Fig. 5 depicts the textural, structural and morphologic properties of the nanocomposite prepared by the colloidal method. The N_2 adsorption–desorption curve is also a type IV isotherm, characteristic of mesoporous materials (Fig. 5a) indicating that the mesoporosity is conserved during the incorporation of ZnO. The surface area and pore size of the sample are $780 \text{ m}^2/\text{g}$ and 2.7 nm , respectively (Fig. 5b). No diffraction peak can be observed in the Small-angle XRD pattern within the 2θ range of $1.0\text{--}5.0^\circ$ (Fig. 5c). As the pore size distribution is quite narrow, the absence of diffraction peak is assigned to the lack of contrast between the silica walls and the channels filled with the ZnO nanoparticles (5 wt.% loading). The micrographs taken by scanning electron microscopy show spherical particles of $\sim 5 \mu\text{m}$ in diameter (Fig. 5d).

The PL spectrum presented in Fig. 3b shows two broad PL bands and a narrower one in the range of 2.5–5.5 eV. After a Gaussian decomposition, four bands at 3.0, 3.2, 3.8 and 4.3 eV can be observed. Two contributions of mesoporous silica can be recognized at 3.0 and 4.3 eV. Usually, a contribution centered at 4.0 eV is also present but may have disappeared in our case due to the contact of the CMI-1 matrix with methanol during the incorporation process. On the other hand, the very narrow peak centered at 3.2 eV is attributed to ‘big’ ZnO nanoparticles grown on the external surface of the CMI-1 matrix. The last PL band, a broad band at 3.8 eV, is thought to come from ‘small’ nanoparticles grown inside the channels of the mesoporous silica materials and which exhibit a relatively

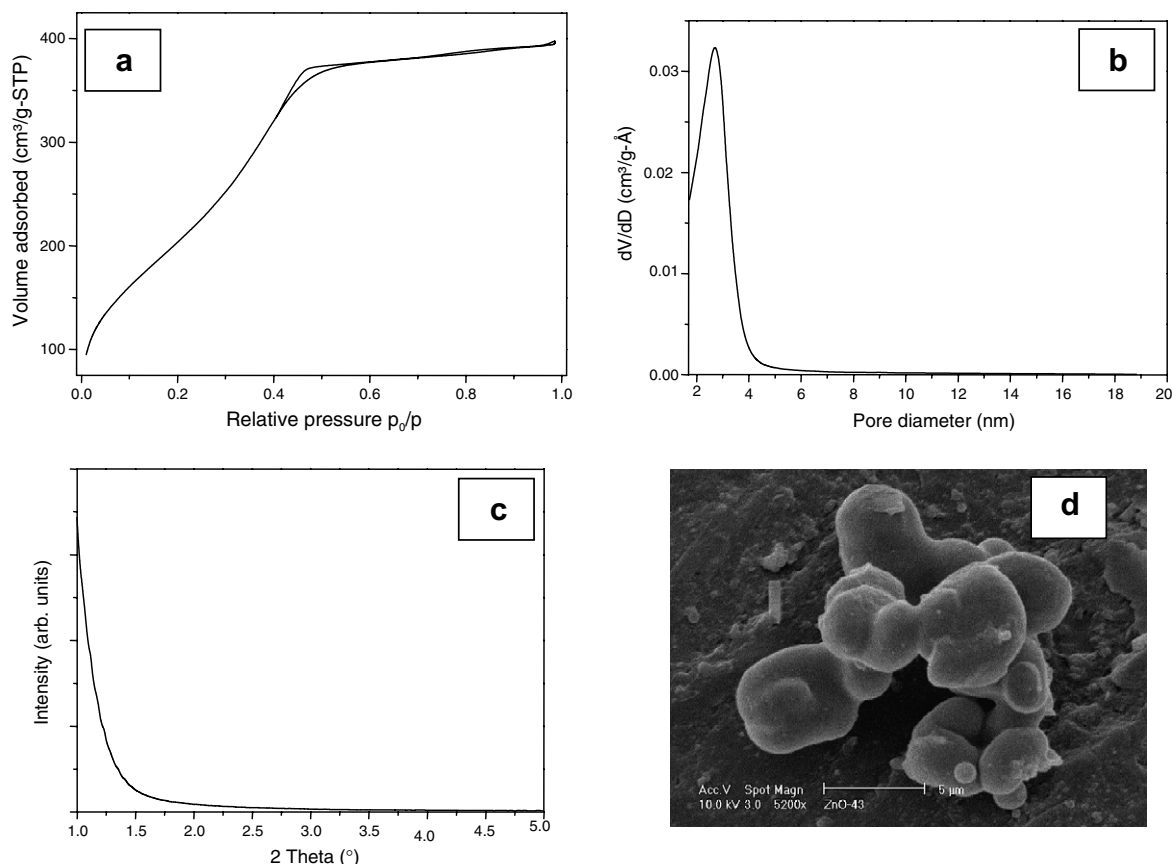


Fig. 5. Textural (a) and (b), structural (c) and morphologic (d) properties of ZnO/mesoporous silica prepared by the colloidal method.

important blue shift due to the expected quantum size effect. This part of the work suggests that the colloidal preparation method can also give a better control of ZnO particle size.

4. Conclusion

The preparation of ZnO/mesoporous silica is achieved by the colloidal and the reverse micelle methods. Both methods lead to nanocomposites exhibiting strong quantum size effect due to the very small particle size of ZnO included in the silica matrix. These methods can be efficient in the preparation of short wavelength (blue) laser nanocomposites.

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